UNCLASSIFIED

AD-A244 166

REPORT DOCUMENTATION PAGE

1b. RESTRICTIVE MARKINGS	
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE	3. DISTRIBUTION / AVAILABILITY OF REPORT: Approved for public release; distribution unlimited
4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S): 91 0032
6a. NAME OF PERFORMING ORGANIZATION: Physics Department, University of Wisconsin-Milwaukee / 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION: Air Force Office of Scientific Research
6c. ADDRESS (City, State, and ZIP Code): P.O. Box 413, MIlwaukee, WI 53201	7b. ADDRESS (City, State, and ZIP Code): Bolling AFB, Building 410, Washington, DC 20332-6448
8a. NAME OF FUNDING / SPONSORING ORGANIZATION: Air Force Office of Scientific Research / 8b. OFFICE SYMBOL (If applicable): AFOSR	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: AFOSR-88-0288
8c. ADDRESS (City, State, and ZIP Code): Same as 7b	10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
61102F	2304	A9	

11. TITLE (Include Security Classification)

Shift Operator Matrix (SOM) Method and Its Application to Chemical/Physical Systems

12. PERSONAL AUTHOR(S)

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13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Final Report	FROM 1 Aug 88 TO 31 Jul 91	26 Aug 91	16

16. SUPPLEMENTARY NOTATION

17. COSATI CODES		
FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

lattice statistics, magnetic susceptibility, phase diagrams, Ising lattices, adsorption, multilayer, magnetization, heat capacity, adsorption

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

We have developed methods to generate the transfer matrices appropriate to the statistical/thermodynamic treatment of systems consisting of particles of any size shape or density, distributed on lattice spaces of any cell-shape, dimensionality and configuration.

Based on this method, we have calculated the configurational heat capacity signatures of several lattice spaces, the adsorption isotherms for planar and cylindrical lattices and the magnetic properties of square- and hexagonal-cell lattice spaces.

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT: ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION: Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL: Dr. Arje Nachman	22b. TELEPHONE (Include Area Code): (202) 767-5025 / 22c. OFFICE SYMBOL: NM

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

UNCLASSIFIED

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91 1227 098

Final Report

for

AFOSR Grant No. 88-0288

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26 August 1991

1. Accomplishments

During the last three years under AFOSR Grant No. 88-0288 we have conducted research that has lead to a new understanding of the statistical/thermodynamic properties of lattice spaces that has resulted in the following:

(A) the publication of the following thirteen (13) articles

"Comparison of Physical Adsorption Isotherms for Planar and Cylindrical Lattices", J. Chem., Phys. 89, 2292 (1988).

"Exact Composite Shift Operator Matrices for Two-Dimensional Ising Lattices", Prog. Theo. Phys. 80, 78 (1989).

"Nearest Neighbor Lattice Statistics on Semi Infinite Two-Dimensional Rectangular Lattices of Various Widths", J. Math Phys. 30, 1380 (1989).

"Transverse Magnetization and Magnetic Susceptibility of Two-Dimensional Ising Lattices", Physica A 158 740 (1989).

"Constant Coverage, Configurational Heat Capacities for Two-Dimensional, Square-Cell Lattices", J. Phys. and Chem. Sol. 50 1051 (1989).

"Shift Operator Matrices for the Nearest Neighbor Problem in Two-Dimensional Hexagonal-Cell Lattices", Physica A 163 863 (1990).

"Shift Operator Matrices for Three-Dimensional Cubic-cell Lattices", Physica A 169 342 (1990).

"Thermodynamic Properties of a Two-Dimensional Nearest-Neighbor Interacting Lattice Gas", Physica A 171 325 (1991).

"Constant Coverage, Configurational Heat Capacities for Two-Dimensional Hexagonal-Cell Lattices", J. Phys Chem Solid (accepted).

"Transfer Matrices for First, -Second- and Third-Neighbor Interactions on Two-Dimensional Hexagonal-Cell Lattices", Physica A (accepted).

"Transfer Matrix Size Reduction Through Symmetry Considerations", Physica A (accepted).

"Submonolayer Magnetization and the Spin Lattice Gas Model", Phys. Rev. Lett. (submitted).

"Anomalous Transverse Magnetic Susceptibilities for Hexagonal-Cell Ising Lattices", (in preparation).

(B) the presentation of the following five (5) seminars/colloquia on the SOM method and its application

Department of Physics, Villanova University, 19 Nov 1988

<u>The Shift Operator Matrix Method</u>

36th Midwest Solid State Conference, Purdue University 10 Oct 1989

<u>Transverse Magnetization and Magnetic Susceptibilities for Square-cell Planar and Cylindrical Lattice Spaces</u>

AFOSR Molecular Dynamics Conference, Captiva Island, Florida 20 Oct 1989

<u>The Statistical/Thermodynamic Properties of Hexagonal Cell Lattice Spaces</u>

Argonne National Laboratories, Argonne, Illinois 15 Nov 1990

<u>The Magnetic Properties of Hexagonal-Cell Lattices</u>

Spring Meeting of the American Physical Society - Cincinnati, Ohio 18-22 March 1991

<u>Multi-layer lattice systems</u>

(C) the education of the following young mathematicians/scientists

(i) J.M. Maeder

M.S. Thesis: "Nearest Neighbor Lattice Statistics on Semi-Infinite, Two-Dimensional Rectangular Lattices of Various Widths"
Published: J. Math. Phys. 30, 1380 (1989)

Mr. Maeder is currently working on his PhD in physics at the University of Minnesota. He is studying the adsorption of ozone using our statistical techniques.

(ii) K. Wu

M.S. Thesis: "Next Nearest Neighbor Interaction on Two-Dimensional Lattice Spaces"

Mr. Wu is now at the University of Michigan working on his PhD. He is currently expanding his work on next nearest neighbor statistics.

(iii) J. Li

Ph.D. Thesis: "Multilayer Adsorption"

In addition Mr. Li has been co-author on the following articles:
"Thermodynamic Properties of a Two-Dimensional Nearest Neighbor Interacting Lattice Gas," Physica A (accepted)
"Transfer Matrix Size Reduction Through Symmetry Considerations," Physics A (accepted)
"Submonolayer Magnetization and the Spin Lattice Gas Model" Phys Rev Lett (submitted)

Mr. Li is expected to receive his PhD in August of 1991.

(iv) K.A. Ibrahim

M.S. Thesis: "Thermodynamic Properties of 2D, Hexagonal Cell Lattices"

(v) C. Zhong

M.S. Thesis: "Anomalous Transverse Magnetic Suscepti-

bilities for Hexagonal-Cell Ising Lattices"

If support can be obtained, Mr. Zhong expects to continue his work for a PhD, working in this area.

(D) the interaction with the following people and organizations

(i) The scientists at the Materials Science Division of the Argonne National Laboratory have requested that we use our SOM technique to study the magnetic (thermodynamic properties of epitaxially deposited films of iron on palladium (100))

(ii) We have contacted the Microsoft Corporation in an attempt to obtain graduate student support. These negotiations are still in progress

(iii) As a result of our publications in this area, we have been in contact with various research groups who have used our work as a take-off point for their own efforts. These include:

a. A.J. Phares, Villanova University

b. F.J. Wunderlich, Villanova University

c. Franco Battaglia, II Universita -Tor Vergata Rome

d. Young Sik Kim, University of Rochester

e. Thomas F. George, SUNY Buffalo

2. Background

Under the AFOSR grant we have developed the shift operator matrix (SOM) formalism to a degree that it can yield transfer matrices (and hence the partition functions) appropriate to a variety of lattice-particle systems. An exploitation of the SOM mathematical formalism has permitted us to examine the statistical/thermodynamic properties of systems of particles having any shape, orientation, density and range of interaction which are distributed on a lattice space of any size, structure or dimensionality.

To discuss our activities with more specificity, it is advantageous to subdivide them into two main categories:

(A) mathematical formalism

(B) applications

A Mathematical formalism

We have shown [1-4] that the eigenvalues of an SOM provide the information necessary to determine the partition function, and hence all the thermodynamic variables and response functions for lattice-particle systems. It follows that the fundamental problem becomes the development of a formalism that allows one to determine the matrix elements of the appropriate SOM. In this regard, we have calculated the SOM matrix elements for systems involving

(i) particles of various shapes [5]

(ii) particles that experience first, second and third neighbor interactions [1,3,6]

(iii) lattice spaces of two and three dimensions for planar, cylindrical, toroidal and rectangular parallelepiped configurations [7,8]

(iv) lattice spaces having square-cell and hexagonal-cell structure [1,4,6]

In addition, we have been able to code the activities which constitute the matrix elements of the SOM so that it is possible to identify the position of a particle on a planar lattice [relative to a lattice edge] as well as the position and orientation of nearest and next nearest neighbor pairs. It is also possible to separate the statistical contribution of circumferential nearest neighbor pairs from the contribution of longitudinally oriented pairs [8,11] for a cylindrical lattice.

The SOM formalism described above has been stated primarily in terms of the occupation/vacancy of lattice sites. As we have shown, however, the SOM method is appropriate to spin-up/spin-down systems, [9] A-B particles in a binary alloy or even non-physical lattices such as "message-spaces." We have also demonstrated [12] that the SOM can be modified so that it can be used to treat any number of different kinds of particles, spins, etc., so that one can treat interaction regimes that are more complex than the three types of nearest neighbor pairs interaction encountered in simple particle/vacancy systems. Such modifications also permit studies of various Potts models [13,14] and Heisenberg models. [15]

A method, based on symmetry considerations [10] has been

developed by which the size of the transfer matrix appropriate to an M x lattice with periodic boundary conditions can be reduced by a factor of up to M^{-1}. Since the computational time required to obtain the eigenvalues of these matrices is of the order of [lattice size]^3, the reduction decreases the computing time necessary for such calculations by approximately M^{-3}. This has permitted us to carry out numerical calculations for larger two-dimensional lattices and to attack multilayer lattice systems.

B Applications

In addition to developing the mathematical formalism described above, we have utilized the SOM-generated transfer matrices to treat both monolayer and multilayer lattice gas systems as well as magnetic (spin) systems.

We have constructed shift operator matrices which permit us to study systems consisting of simple, nearest-neighbor-interaction particles distributed on planar M x N, square-cell lattices. [8] Such SOM's are transformed into the corresponding SOM's for cylindrical lattices of the same dimension. Utilizing these SOM's, we have calculated and contrasted the physical adsorption isotherms for M x planar lattices [with two free edges] and for cylindrical lattices [having no free edges] of the same dimensions. The calculations cover the entire range of temperature, chemical potential, particle-particle interaction potential and are carried out for several values of M.[12] By modification of the SOM for planar lattices, we have shown, explicitly that the differences between the physical adsorption isotherms for these two kinds of lattices are reflective of

anomalous surface particle densities along the free edges of the planar lattice. [8,11]

Utilizing shift-operator-matrix-generated transfer matrices, we have calculated [11] the configurational, constant area, constant coverage heat capacity signatures for semi-infinite [M x] planar and cylindrical, square-cell lattices as functions of the particle/lattice, and particle/particle interaction potential energies, of coverage for various widths i.e., various values of M. The calculated heat capacity signatures for planar lattices exhibit a behavior not shared by cylindrical lattices.

To investigate these differences, we have modified the SOM for planar lattices so that particles and occupied nearest-neighbor pairs on and near the lattice edges can be distinguished form their counterparts interior to the lattice. We were able to show quantitatively that the coverage and the density of occupied nearest-neighbor pairs along the lattice edges are different from those interior to the lattice and from their averages for the lattice as a whole.[11] Similarly, we have shown explicitly how the position of an occupied nearest-neighbor pair relative to the lattice edge determines its contribution to the overall heat capacity signature of a planar lattice.

When the overall lattice coverage approaches unity (for attractive particle/particle interaction) the heat capacity per particle of a planar lattice exhibits an extremely rapid decrease with temperature. This indicates the exhaustion, internal to the lattice, of vacant nearest-neighbor pairs.

Similar calculations for hexagonal-cell lattices [13] reveal

a richness and complexity in the heat capacity signatures undetected by finite scaling techniques not present in square-cell lattices.[11] For example the temperature rate of change of the density of vacant pairs along lattice edges shows a double sign reversal. In addition the heat capacity signatures of semi-infinite, hexagonal-cell lattices exhibit two maxima; one associated with nearest neighbor pairs that reside along lattice edges and the other with particle pairs internal to the lattice.

Other investigators [16,17] have used our results for the square-cell, 2 x N lattice [referred to in the literature as the McQuistan-Hock model] to obtain analytic, closed-form heat capacity signatures. When these results are applied to adsorbed systems for which the particle/particle interactions dominate the particle/substrate interactions the computed temperatures at which the heat capacities display their maximum are in excellent agreement with experimentally measure critical temperatures.

Employing the shift operator matrix (SOM) method to obtain the necessary partition functions we have calculated and compared the transverse, antiferromagnetic magnetization and magnetic susceptibility [as functions of temperature, applied magnetic field and spin-spin interaction potential] for a system of nearest-neighbor-interacting, classical, spin-1/2 particles distributed on M x (M=2,3,4...) planar, square-cell lattices (having two free edges) and cylindrical lattices (having no free edges).[9]

Our calculations of the transverse, antiferromagnetic magnetization and magnetic susceptibility of planar lattices show explicitly the influence of the lattice edges. For square-cell

cylindrical lattices, the effect of the antiferromagnetic seam is also evident (for odd values of M). The susceptibility for both kinds of lattices depends on the applied field in an anomalous manner which increases with M and which cannot be ascribed to the orientation [relative to the lattice directions] of the nearest-neighbor spin pairs from which ordered spins are derived.

Recent, unpublished calculations for hexagonal-cell lattices have yielded magnetic susceptibility signatures that are exceedingly complex. For example, the zero field-susceptibility can be either a minimum or a maximum, depending on lattice size. In addition, the shape of the susceptibility vs field curves exhibit asymmetries that also changes with lattice size. We have tentatively explained such anomalous behavior in terms the relative degeneracies directly obtained from the SOM but additional work is needed in this area. In particular, the magnetization signatures of planar lattices are very complicated and not understood.

The matrix size reduction techniques discussed above [10] have permitted us to treat multilayer systems. We have been able to calculate the isotherms for multilayer adsorption and to determine the thermodynamic response functions for systems consisting of up to three layers.

Experimental researchers at the Argonne National Laboratory have been studying the magnetic properties of epitaxially grown monolayer and submonolayer films of iron on palladium (100) (18-21). Such films exhibit a remarkable series of properties including 2D magnetism, phase transitions, critical behavior, enhances magnetic moments, transverse surface magnetic anisotropy

and the existence of new phases, stabilized by epitaxy. *In situ* measurements of these films, particularly the surface magneto-optical Kerr effect (SMOKE) investigations of Fe/Pd(100), indicate a coercivity, Kerr intensity, Curie temperature and magnetization that depend on the iron coverage of the Pd(100) substrate. Of particular interest is the dramatic T_C variation with coverage in the submonolayer region.

It has been pointed out that these 2D magnetic systems have an Ising-like character [16]. As such, their properties can be studied in an insightful manner by the techniques, involving the SOM method, which we have developed.

We have performed preliminary studies of a simple, "three particle" submonolayer system [spin-up, spin down and vacancy] and have obtained interesting results which indicate

(a) (Fig 1) a magnetization vs. reduced temperature for various values of the submonolayer iron coverage, that is in good agreement with experimental results. In particular this agrees with the long, high-temperature tail experimentally observed.

(b) (Fig 2) an extremely interesting constant area, configurational heat capacity vs. reduced temperature for various values of the submonolayer iron coverage that exhibits a double maximum.

(c) (Fig 3) a Curie temperature as a function of the submonolayer iron coverage (solid circles) that is quite similar to experimentally obtained curve (open squares).

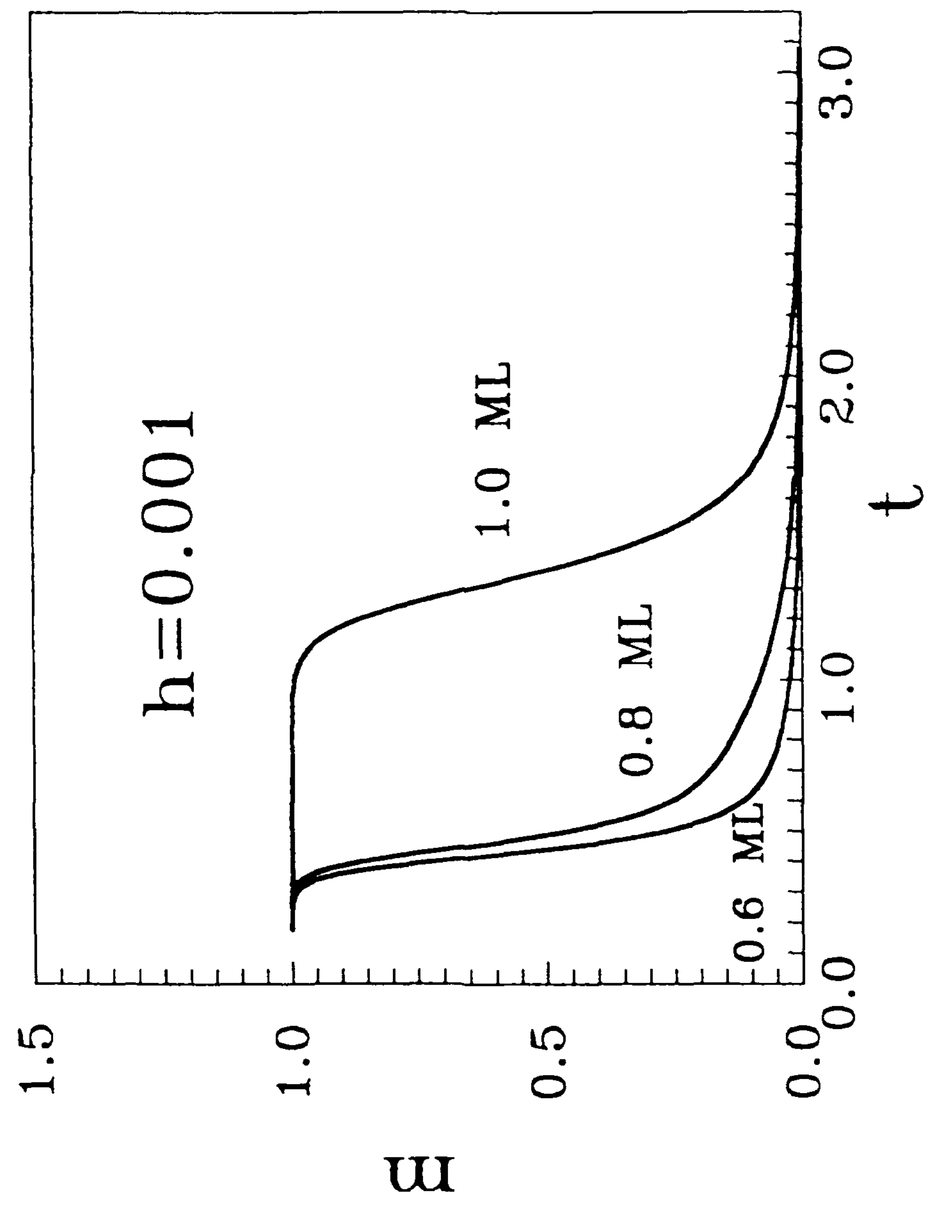

Fig. 1

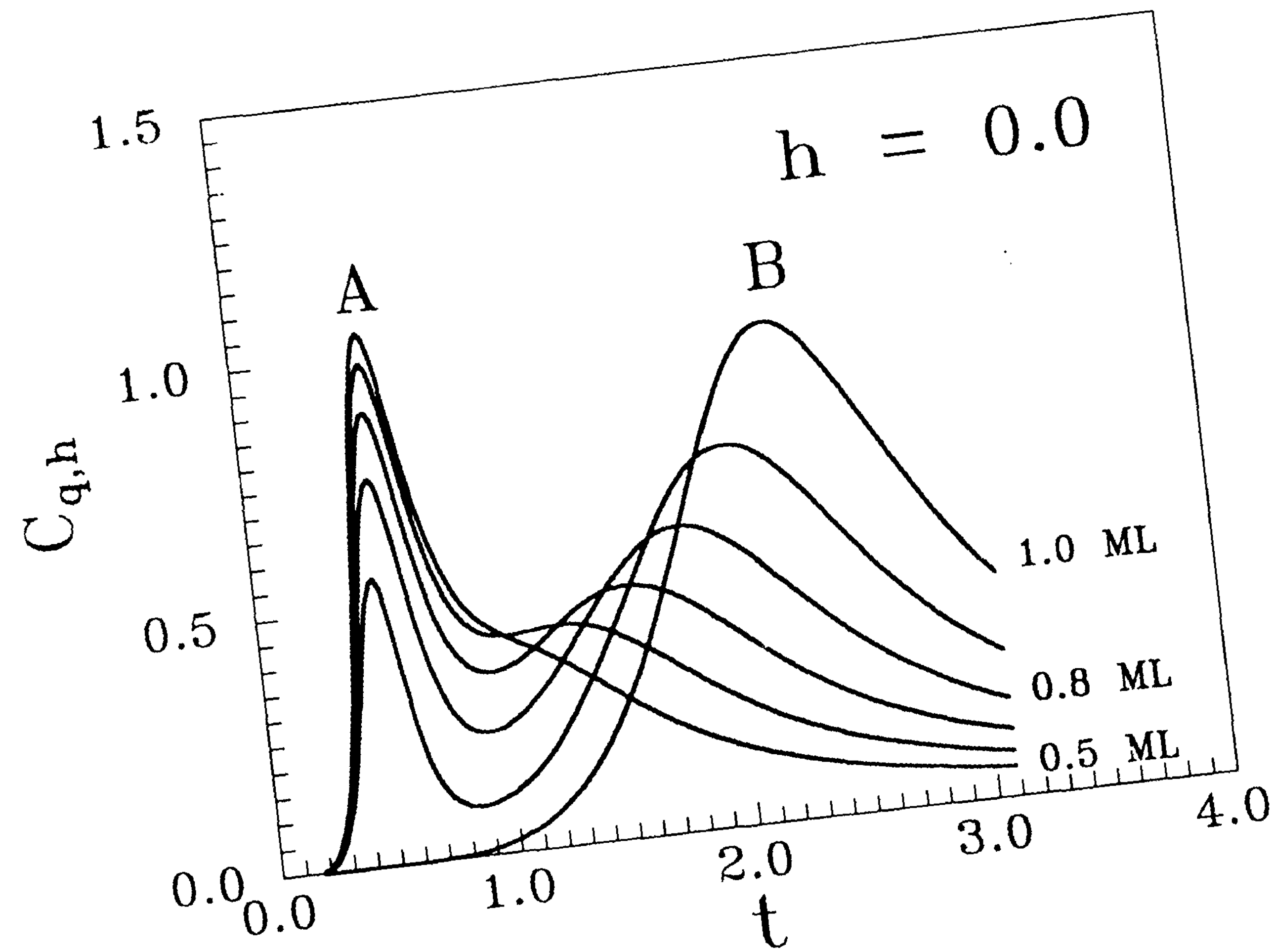

Fig. 2

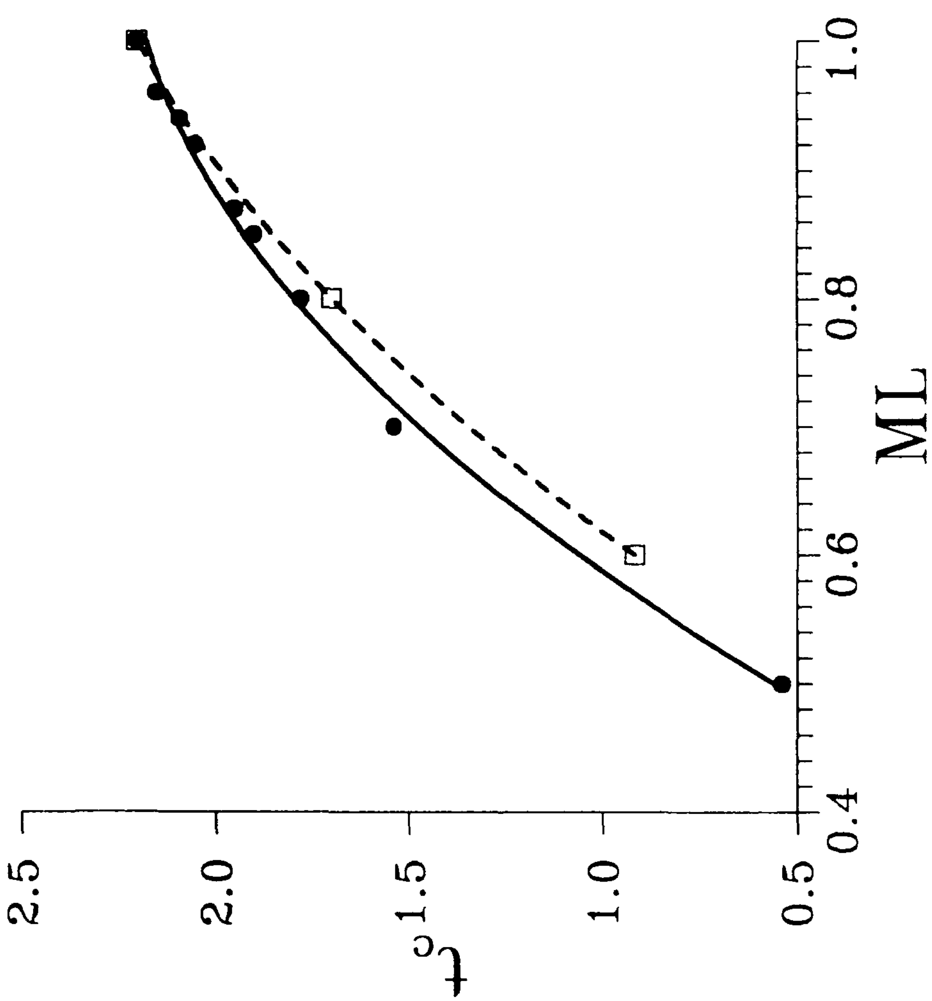

Fig. 3

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